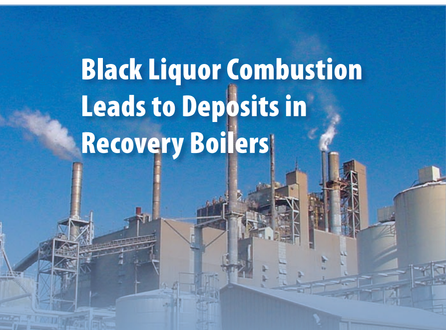
SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

Celebrating 25 Years 1979-2004

CRF NEWS

COMBUSTION RESEARCH FACILITY

May/June 2004 • VOL. 26, NO. 3



Black Liquor Combustion Leads to Deposits in Recovery Boilers

The primary role of a pulp mill recovery boiler is to recover the caustic sodium and sulfur compounds used to extract the cellulosic pulp from the biomass feedstock (typically wood chips) in a chemical digester. These compounds are reused in the pulp-making process. The boiler's secondary role is to produce electricity and steam energy for the pulp mill.

The fuel burned in recovery boilers is a concentrated residue from the chemical digesters known as "black liquor." This viscous solution is composed of nearly equal parts biomass extractives, sodium and sulfur compounds, and water. Black liquor is introduced into the furnace as a coarse spray with a mean drop size of several millimeters. The large drops dry and devolatilize, and the remaining char particles fall down to the bottom of the furnace, where they land on a char bed. The char continues to react in the char bed, oxidizing the carbon while reducing the inorganic compounds to a molten smelt.

Combustion of black liquor results in substantial sodium vaporization and the generation of a dense, submicron sodium sulfate fume in the upper furnace. In addition, some small char particles are produced and carried, or entrained, upward in the furnace flow, producing large (~ 1 mm) "carryover" particles that deposit on the first tube banks (i.e., the superheater) in the boiler. Until recently, little attention was paid to entrained particles in between these two characteristic sizes.

Sandia National Laboratories

Tackling Boiler Buildup

Laser Particle Measurements Improve Understanding of Deposit Formation in Pulp Mill Recovery Boilers

Recovery boilers in pulp mills are plagued by deposits that can foul heat transfer surfaces and plug the boilers. Efforts to study a class of particles suspected in playing a key role in deposit formation have been problematic due to the hostile boiler environment and the difficulty in measuring the particles without interference from submicron fume particles.

Researchers at the CRF and Process Metrix recently performed the first laser-based, in situ measurements of the suspect particles in two operating recovery boilers. The intermediate-sized particles (ISPs) range in size from 2 to 100 micrometers (see Figure 1). By providing accurate measurements of ISP particle size, concentration, and chemical composition, the laser measurements have provided important information for recovery boiler design and operation.

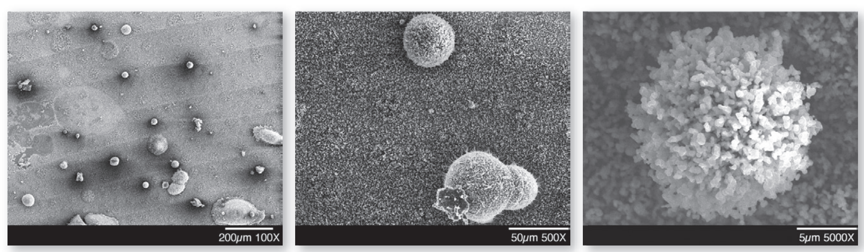


Figure 1. SEM photomicrographs of ISP particles captured on an impaction plate during a 10-s exposure in front of the superheater at the Longview, Wash., boiler. The magnification of the images increases left to right from 100X to 500X to 5000X, with corresponding length scales of 200µm, 50µm, and 5µm.

The recently completed project was sponsored by the Department of Energy's Industrial Technologies, Industries of the Future Program, with additional funding provided by Weyerhaeuser Company and International Paper Inc., two of the world's largest pulp and paper companies. Chris Shaddix was the project leader for Sandia, while former Sandia researcher Don Holve led the project for Process Metrix, where he serves as senior vice president.

Isolating ISPs

Until recently, the pulp industry and its associated research community paid little attention to the role of ISPs in the formation of boiler deposits. Preliminary work indicated their potential importance and demonstrated that they formed during black liquor drop combustion and char bed burning (see sidebar), but extractive boiler sampling gave inconsistent results, because of interference from sodium fume particles.

The researchers adapted two laser diagnostic approaches for use in recovery boilers: a single-particle counting technique, developed by Process Metrix, and laser-induced breakdown spectroscopy (LIBS), a chemical measurement technique tailored by Sandia researchers for interrogating entrained particles.

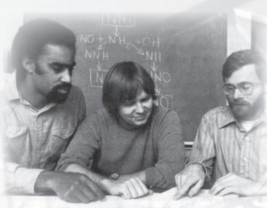
The single-particle counter uses a low-power diode laser and measures the forward-scattered light pulse from individual particles passing through the focus of the laser beam. Mean velocity, overall concentration, and size distribution of the particles are determined

(Continued on page 6)

25 Basic Energy Sciences MILESTONES AT THE CRF

1978 Groundbreaking held for construction of Combustion Research Facility

1979-1981 CRF researchers and collaborator develop a reaction mechanism for THERMAL DeNOx™, in which ammonia is added to combustion products to reduce the pollutant nitric oxide to molecular nitrogen and water. Their work increases understanding of the elementary chemical reaction steps responsible for the reduction process.



1980 CRF opens to visiting researchers.

1981 Dedication of CRF held.

1982 CRF researchers significantly enhance the spatial resolution and sensitivity of coherent anti-Stokes Raman spectroscopy (CARS) for use in combustion studies. Their improved CARS method is used to study detailed temperature profiles and to detect carbon monoxide concentrations in a small diffusion flame, studies that would have been extremely difficult to do using conventional CARS.

A CRF scientist becomes one of the first researchers in the world to recognize the potential usefulness of multiphoton excitation for detection of atomic flame radicals such as hydrogen and oxygen. The technique's primary benefit is the avoidance of photochemical interference.

1980s-early 1990s
CRF researchers make extensive, precise kinetic measurements on hydroxyl radical (OH) reactions with alkanes and alkenes. Knowledge of the rates and product distributions for OH reactions is crucial to modeling combustion chemistry. This work continues to be used extensively today.

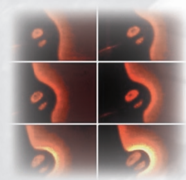
1989 CRF researchers publish "Mechanism and Modeling of Nitrogen Chemistry in Combustion" in *Progress in Energy and Combustion Science*; becomes one of the most frequently cited papers in the field of combustion.

1994 CRF-led team solves difficult problem of measuring ultrashort laser pulses, an important capability in laser diagnostics. Using a technique they created called frequency-resolved optical gating (FROG), researchers measure a "spectrogram" of the laser pulse, analogous to a musical score of a sound wave.

1996 First International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames held in Naples, Italy. Workshop arose out of Sandia's collaborations with experimental and computational researchers worldwide on turbulent nonpremixed and partially premixed combustion and includes an online library of well-documented flames for use in model validation and the advancement of basic scientific understanding of turbulent combustion. Workshop is held biennially in conjunction with the International Symposium on Combustion.

New turbulence modeling strategy is developed that captures key mechanisms of multidimensional turbulent flow with a one-dimensional description. Called the one-dimensional turbulence (ODT) model, the strategy reproduces many known features of turbulence microstructure and macrostructure, unifying them within a common modeling framework.

1996-present
Planar imaging experiments provide detailed and reproducible experiments for testing models and developing novel diagnostic techniques, such as imaging of chemical reaction rates, a technique that was first demonstrated in 1998. The experiments are closely coupled with numerical simulations.



1978 | 1980 | 1985 | 1990


Combustion Research Facility NEWS

CRF NEWS LAUNCHED—

BES REVIEWS SANDIA COMBUSTION RESEARCH

CONSTRUCTION UNDER WAY ON CRF

1979 A general-purpose, chemical kinetics computer code package called CHEMKIN™ is completed. CHEMKIN was born out of the need for a more efficient way of solving combustion problems involving complex series of chemical kinetics phenomena.

Bimonthly newsletter called *Combustion Research Facility News* is launched.

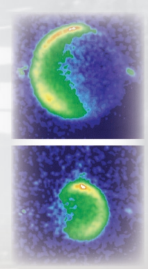
Turbulent Diffusion Flame Facility becomes operational. The facility provides a well-characterized, controlled flow field for flames of practical size and permits the use of nonintrusive optical diagnostic techniques.

1986 Paper published in *Nature* on a new technique for removing nitrogen oxides (NOx) from exhaust gas streams. The process, called RAPRENOx (Rapid Reduction of Nitrogen Oxides), reduces NOx in diesel exhaust streams from 440 ppm to less than 5 ppm in demonstration tests.

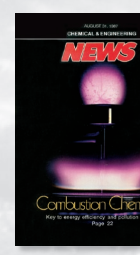
1987 CRF researchers publish a special 24-page report entitled "Combustion Chemistry" in *Chemical and Engineering News*, at the invitation of editors.

1987 Paper published in *Journal of Physical Chemistry* on the ion imaging technique, a way of measuring the velocity of slowly moving ions. This technique produces a two-dimensional velocity map or "snapshots" of molecules colliding or splitting during a chemical reactions. Analysis of the snapshots provides detailed information about bond strengths and velocities of the reaction products. Not just for studying combustion, the laser-based technique and apparatus have since been replicated in more than 40 laboratories worldwide.

RAPRENOx process for removing nitrogen oxides from exhausts gases is honored by *R&D* magazine as one of the 100 most significant new technical products of 1986.



1997 CRF researchers pioneer the use of cavity ringdown spectroscopy for quantitative species measurements in flames. The technique allows pulsed lasers to be used for the first time for sensitive, quantitative absorption measurements, free from quenching and other collisional effects.



CRF-led team observes the first laser-indu
trum of the ketenyl radical (HCCO), an imp
hydrocarbon combustion. Characterization
dynamics of HCCO provides fundamental d
to test its potential as a molecular marker i

1997 CHEMKIN™ licensed to San Diego-b
provides technical support and upgrades t
has evolved into a software suite used wor
combustion, and chemical processing indu

CRF a World Leader in Using State-of-the-Art Measurement and Computational Tools to Advance Fundamental Understanding of Combustion

Facility Marks Many Milestones from 25 Years of DOE Investment in Basic Research

This is the second in a series of articles commemorating the CRF's 25th anniversary. Bill Kirchhoff, former program manager for chemical physics in the Department of Energy Office of Basic Energy Sciences, looks back at the CRF's basic research program, which he oversaw until he retired in January. Future guest articles will address other aspects of the CRF's research.

Combustion produces nearly 85% of the nation's energy and a significant amount of its emissions, making the design of more efficient, less-polluting combustion devices an ongoing national priority. It should be obvious to all that progress in what is arguably a "mature" technology can only be accomplished by means of combustion models of high fidelity and proven reliability. The development of such models continues to call for advances at the forefront of science and technology. To this end, scientists at the Combustion Research Facility use the most advanced techniques of measurement, theory, and computational science to probe the extraordinary complexities that characterize all combustion phenomena. This work, carried out in a collaborative research environment, has been supported in part by the Department of Energy Office of Basic Energy Sciences (BES), throughout the CRF's history (see timeline below).

Bill Kirchhoff

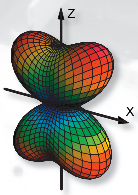
The chemistry of combustion consists of dozens of species and hundreds of reactions. Most of the species are unstable, transitory molecular fragments whose detection challenges the most advanced analytical techniques. The majority of these reactions will never be observed experimentally. At the most fundamental end of the BES-supported CRF research portfolio, scientists are engaged in experimental and theoretical molecular dynamics, with the aim of calculating the properties of reactions and species that elude measurement. A basic research program in chemical kinetics provides insight into combustion chemistry, data for inclusion in combustion models, and the validation of theoretical and computational predictions of reaction rates.

The interaction of chemistry with fluid dynamics, particularly turbulence, renders even more difficult the computational characterization of combustion devices. The CRF's flame laboratories and advanced imaging laboratories provide the means for characterizing the interaction of turbulence with chemistry through the simultaneous measurement of multiple species, flow velocities, and temperature, and through the precise generation of flame geometries. A growing effort in advanced combustion modeling provides proven mathematical approaches and direction for the experimental program. These laboratories are known worldwide and have spawned the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames, which has done much to allow at last the rationalization of measurements between laboratories and meaningful comparisons between measurement and theory.

The collocation of basic and applied research at the CRF allows each to inform and inspire the other, and the DOE's energy technology programs have benefited as a result. The breadth of the research portfolio and the elegance and finesse of scientific tools employed are truly impressive. But it is the excellence of the CRF's scientific staff, recognized throughout the world, that has enabled the facility to maintain its leadership for the past 25 years and has made support by the DOE a wise investment for the future.

1995 **2000** **2004**

1998 New technique and apparatus combines femtosecond lasers with three-dimensional ion and electron imaging to study the dissociation of molecules a single molecule at a time. Such events typically occur in femtoseconds (one millionth of a billionth of a second). The technique can be used for the validation of predictive models and theories of chemical reactions.



ced fluorescence spec-
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n combustion systems.

1999 Dedication of Phase II adds 20,000 square feet of laboratories and nearly 9000 square feet of offices to CRF.

based Reaction Design, which
o CHEMKIN customers. CHEMKIN
ldwide in the microelectronics,
ustries.

1999-present CRF develops picosecond laser that offers a unique combination of time and spectral resolution. Picosecond pump-probe experiments enable a detailed understanding of collisional phenomena. High-power, relatively low energy pulses enable efficient nonlinear excitation, potentially reducing photolytic interference.

2001 Using direct numerical simulation—a computational modeling tool—CRF researchers showed the importance of turbulence-chemistry interactions in autoignition. Autoignition, particularly at high pressures, is poorly understood but plays an important role in diesel engine technology.

2002 CRF researchers develop master equation methodology for treating reactions that occur over multiple interconnected potential wells, critical to understanding polycyclic aromatic hydrocarbons and soot formation.

2002-present
Collaborative team uses a new flame-sampling molecular beam mass spectrometer and Lawrence Berkeley Lab's Advanced Light Source to study fundamental flame chemistry.

2003 CRF researchers develop a way of quantifying uncertainty in reacting flow computations. Results demonstrate uncertainty quantification (UQ) in one-dimensional hydrogen-oxygen flame computations. UQ analysis accounts for propagation of uncertainty in model parameters to predictions, and is necessary for model validation with respect to empirical observations and for design optimization.

Two CRF researchers provide the first complete theoretical treatment of the propargyl + propargyl reaction. Earlier research by a CRF research team demonstrated that this reaction is a key cyclization step in forming polycyclic aromatic hydrocarbons and soot in flames.

2004 Researchers at the CRF and Columbia University create extremely cold molecules that could be used as the first step in creating Bose-Einstein molecular condensates. Their technique uses a collision between a molecule and an atom in a crossed molecular beam.

New Comanager of Microfluidics Department Appointed

Yolanda Fintschenko is the new comanager of the Microfluidics Department in the Combustion & Physical Sciences Center. Fintschenko will lead research efforts in the group, while comanager Art Pontau will focus on growing commercialization efforts.

Fintschenko has a background in bioanalytical chemistry and has been at Sandia for five years, following a short fellowship in the Netherlands. She received her doctorate from the University of Kansas. Her most recent work focused on the development of a selective concentrator for water-borne pathogens (see below). Fintschenko has led several projects and been an active leader in technical conferences.

Analytical Chemistry Features Water Pathogen Detection Research

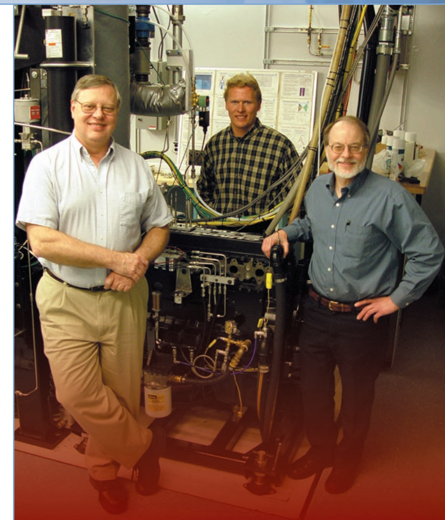
The March 15 cover of *Analytical Chemistry* featured Sandia research on a new approach for selectively isolating and concentrating dead and live *E. coli* in water in a single step (see also *CRF News*, November/December 2003). The method, which uses insulator-based dielectrophoresis, reduces the sample volume needed to successfully deliver a detectable amount of pathogenic material to an analytical device. The research, by Microfluidics Department scientists Blanca Lapizco-Encinas, Blake Simmons, Eric Cummings, and Yolanda Fintschenko, was also featured as a "research profile" in the journal's April 1 issue.

Diagnostics and Reacting Flow Research Reviewed

BASIC ENERGY SCIENCES

The CRF's diagnostics and reacting flows research, supported by the Department of Energy Office of Basic Energy Sciences, underwent peer review in March. Five reviewers from various universities spent three days at the CRF hearing presentations and meeting one-on-one with researchers. Shown left to right: Sarah Allendorf (CRF), Richard Miles (Princeton University), Bob Carling (CRF), Eric Rohlfing (DOE), Andy McIlroy (CRF), Bill McLean (CRF), John Buckmaster (University of Illinois, Urbana-Champaign), James Hermanson (University of Washington), Marcus Aldén (Lund University), and Godfrey Mungal (Stanford University).

Alan Kerstein presents his research on high-energy processes to the review panel.



Nicholas Cernansky (left), a mechanical engineering professor at Drexel University, has completed a six-month sabbatical at the CRF, working with Sandians John Dec (right) and Magnus Sjöberg (center) on homogeneous charge compression ignition (HCCI) engine combustion. HCCI is a promising new engine combustion concept for high efficiency and ultra-low emissions. Cernansky worked on an investigation of the potential for thermal stratification to extend HCCI operation to higher loads, using a special multizone version of the SENKIN application of CHEMKIN written by Sandian Andy Lutz. The work showed that controlled charge stratification can significantly increase the HCCI operating range, offering a potential solution to one of the obstacles to implementing HCCI in production engines.

Jessico Matto is the CRF's new Visitor Program administrator. She is responsible for a variety of activities involving the CRF's approximately 120 annual visitors, including coordinating visits of foreign nationals and handling housing for short-term visitors. Matto was formerly the assistant editor of *CRF News.*

Contact her at (925) 294-3853, jmatto@sandia.gov.

University, Industry Groups Meet at CRF to Discuss Advanced Low-Temperature Combustion and Diesel Combustion Processes

Two consecutive meetings drew more than 60 people to the CRF in January to present and discuss the latest research on advanced low-temperature combustion and diesel combustion processes funded by the Department of Energy Office of FreedomCAR and Vehicle Technologies.

The first meeting, held Jan. 27–28, included 50 members of the Advanced Engine Combustion (AEC) Working Group, which is composed of representatives from industry and other national laboratories participating with Sandia in a memorandum of understanding (MOU) to pursue research on next-generation engines. MOU participants included representatives from General Motors, Ford, Cummins, Detroit Diesel, Caterpillar, John Deere, International Truck, Mack/Volvo, General Electric, DaimlerChrysler, Sandia, Lawrence Livermore, Los Alamos, Oak Ridge, and Argonne. Also attending were representatives from three universities—Wisconsin, Illinois, and Wayne State—funded by DOE to conduct closely related research.

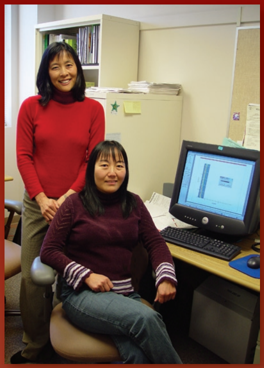
On Jan. 28–29, additional attendees from the University of Michigan, University of Wisconsin, Massachusetts Institute of Technology, and Stanford University joined the group for the University Homogeneous Charge Compression Ignition (HCCI) Engine Combustion Working Group meeting.

Observing Different Reaction Paths in Chemistry

CRF chemists David Osborn and Peng Zou have used time-resolved infrared spectroscopy to measure the contribution of different reaction paths to a single set of products in a chemical reaction. Their research, recently accepted for publication as a "hot article" in *Physical Chemistry Chemical Physics*, calls into question the common assumption that each observed product channel in a reaction arises from a single pathway on the potential energy surface.

Isotopic labeling of the reactants combined with isotope-specific detection is the key to this technique. By studying the labeled $HCC^{16}O + {}^{18}O_2$ reaction, the chemists determined the relative flux through different paths on the potential energy surface leading to a single asymptote, $H + CO + CO_2$. In the labeled reaction, the dominant isotopic products are $C^{18}O$ and ${}^{16}OC^{18}O$. Combined with data from the corresponding reaction in natural isotopic abundance, these results show that at least 85% of the reactive flux passes through a four-membered OCCO ring intermediate. An alternative reaction path through an energetically allowed three-membered COO ring intermediate represents less than 15% of the total reactive flux.

Osborn and Zou's article appears in volume 6, pages 1697-1705, *Physical Chemistry Chemical Physics*. Hot articles, along with author interviews, can be accessed for free from the journal's home page ***www.rsc.org/is/journals/current/pccp/pccppub.htm.***



Postdoc Shiling Liu (seated) has accepted a position at United Technologies Research Center in Hartford, Conn. She had worked with Sandian Jackie Chen (left) for more than two years on numerical simulations of excess enthalpy catalytically assisted micro-combustion and nonpremixed autoignition of n-heptane and hydrogen.

Boilers

(Continued from page 1)

through analysis of the time record of the pulse and by applying a statistical deconvolution algorithm to a large number of scattering events. The LIBS technique uses a high-power, pulsed Nd:YAG laser to form a local spark, or plasma, in the flow and then collects the emitted UV-visible and near-infrared light for analysis of elemental composition with a spectrometer coupled to an intensified CCD camera. For small particles (typically < 10 μm) that are completely decomposed within the plasma, the LIBS technique can provide a quantitative determination of the elemental composition of the particles.

Two Recovery Boilers Used

Sampling was conducted at a recovery boiler in Washington that was characteristic of older recovery boilers and a more modern one in Alabama. In both cases, the single-particle counting technique measured significant quantities of ISP particles in the upper furnace, just before the flow passed through the steam tubes. Past the steam tubes, ISP concentrations were very low, showing that the bulk of the particles had deposited on the tubes. The measurements also showed that ISP concentrations in the upper furnace are highly variable in time (see Figure 2), suggesting that improved control of process variables such as fuel viscosity and air flow distribution may lead to ISP reductions.

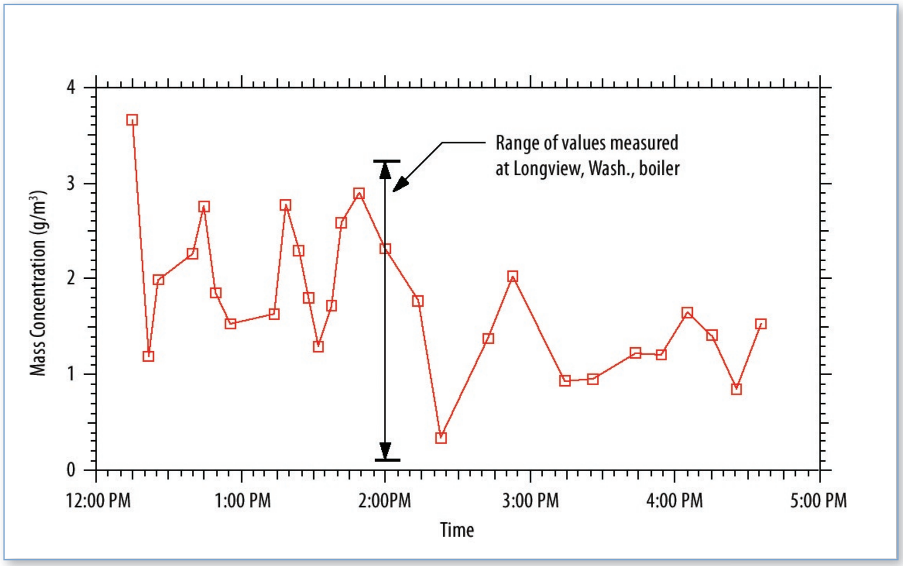


Figure 2. Time history of ISP particulate mass (measured as a five-minute average) at the Courtland, Ala., recovery boiler.

The LIBS measurements showed fairly constant sodium particle concentrations (dominated by fume), but irregular concentrations of trace refractory elements that are not present in the fume. In this way, the chemistry of the ISP particles could be distinguished from that of the fume. Further chemical analysis was provided by scanning electron microscopy (SEM) analysis of the impaction samples, using energy dispersive x-ray spectroscopy (EDX). This analysis revealed that ISP particles have considerably lower potassium, chlorine, and sulfur content relative to fume. With this information, the molten state of the ISP particles, and thus their deposition efficiency, can be accurately predicted through CFD modeling.

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